# High-purity carbon nanotubes synthesis method by an arc discharging in magnetic field

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(Received 4 February 2002; accepted for publication 9 May 2002)

We developed a synthesis method of multiwalled carbon nanotubes (MWNTs), in which an arc discharging was controlled by a magnetic field. Using this method, we can obtain high-purity MWNTs (purity >95%) without purification which disorders walls of MWNTs. The current–voltage measurements show that the carriers would transport ballistically through our defect-free MWNTs with the maximum current density of $\sim 10^{11}$ A/m$^2$. Therefore, our method provides defect-free/high-purity MWNTs as nanosized electric wires for device fabrication. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1491302]

Carbon nanotubes (CNTs) have emerged as an attractive material for electronic applications.[1–6] Specifically, CNTs are suitable for nanosized electrical wires, carrying current densities up to $10^{13}$ A/m$^2$ (Refs. 7–9). The fabrication of CNT devices requires high-purity CNTs. However, purification processes (sonication and annealing) induced disordering the walls of CNTs,[10–14] which would suppress the current density of them. Thus, we require an advanced CNT-growth method, which can provide high-purity/defect-free CNTs without any purification processes. In this work, we found that by using the arc discharging method and applying a magnetic field permits us to synthesize high-purity multiwalled carbon nanotubes (MWNTs). We also measured current–voltage ($I$–$V$) characteristics of obtained MWNTs to evaluate their maximum current densities (current carrying capacities) near electrical breakdown.[15]

Our method is a modified conventional arc discharging one[16] with a magnetic field around the arc plasma. The schematic diagram of our synthesis system is shown in Figs. 1(a) and 1(b). The carbon arc discharging is run between two electrodes (graphite rod, purity >99.999%) in a reaction chamber. To improve the purity of MWNTs in soot, we adjusted the experimental conditions, such as the configuration of the magnets, the graphite rod size, and atmospheres in the reaction chamber. In this letter, we calculated the purity of MWNTs from the areal ratio of MWNTs in scanning electron microscope (SEM) images[17] using an image processing system (OPTIMAS, Optimas Co.). Figure 2(a) shows a SEM image of soot synthesized in air (pressure ~100 kPa) with the symmetrical magnetic field, which was formed around the discharging region by four cylindrical Nd–Fe–B magnets (diameter×height=22 mm×10 mm, magnetic flux density ~300 mT), as shown by Fig. 1(b). The purity of this MWNTs in the soot reached to ~97%. By comparison, soot synthesized without the magnetic field [Fig. 2(b)] consists of not only MWNTs but also a large amount of byproducts (amorphous carbon, graphite particles, and fullerenes). These results show that the purity of the MWNTs would significantly increase by applying the magnetic field. In this experiment, we examined the purity of synthesized MWNTs for various atmospheres (He, Ar, $O_2$, $N_2$, and air, pressure ~100 kPa). We found that the averages of MWNTs purity are ~97% (in air), ~96% (in Ar), ~40% (in He), ~33% (in $N_2$), and ~26% (in $O_2$) for each three soots. Furthermore, we changed the diameter of a cathode to use a thinner one (5 mm in diameter) than an anode (15 mm in diameter), since the thinner cathode can collect MWNTs in the center of the arc. Thus, we succeed in synthesizing high-purity MWNTs as well as ones purifying them by chemical and physical process (sonication, separation, and annealing).

We investigated the effect of the magnetic field for the carbon arc plasma. First, the motion pictures of the arc plasma were taken with a digital video camera (frame rate =30 Hz). Figure 3 shows typical motion pictures of the arc plasma with [Fig. 3(a)] and without the magnetic field [Fig. 3(b)]. The pictures show that the magnetic force would confine the plasma between electrodes so as to suppress the fluctuation of the arc. This phenomenon was observed for 12 experiments under the same condition. Next, we measured optical emission spectra of the arc plasma with a charge coupled device optical spectrometer (S2000, Ocean Optics, Inc.). Applying the magnetic field, a clear peak can be observed in the emission spectrum at a wavelength of 247.9 nm [Fig. 3(c)]. This peak disappeared under the background

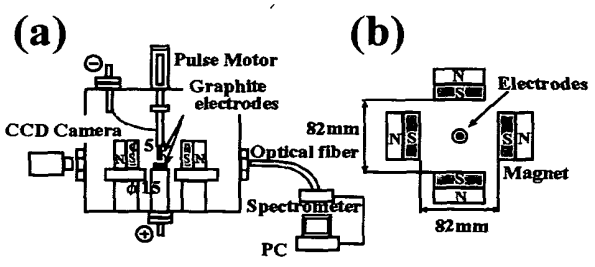


FIG. 1. (a) Schematic diagram of the synthesis system for MWNTs. A cathode (5 mm in diameter) and an anode (15 mm in diameter) were used. During arc discharging, we applied a potential of between the electrodes at ~18 V dc with a typical electric current of ~70 A. (b) Arrangement of four Nd–Fe–B magnets around the electrodes.

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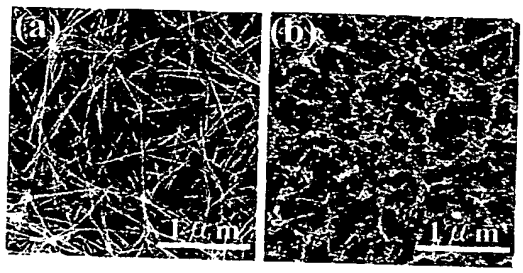


FIG. 2. SEM images of MWNTs synthesized with (a) and without (b) the magnetic field.

without the magnetic field [Fig. 3(d)]. The same spectra were obtained for four experiments. Since this peak was assigned to neutral carbon monomers,[18] the concentration of carbon monomer would increase in the arc plasma with the magnetic field. As previously pointed out,[19] the purity of MWNTs increased by increasing the concentration of the carbon monomer in the arc plasma. The magnetic confinement of the plasma could increase a collision probability between charged particles in the plasma, so that the reaction of the MWNTs growth might be accelerated. Further investigations are needed to clear this point.

In order to measure $I-V$ curves of our MWNT and a commercially purified MWNT (purity ~90%, by arc discharging), we picked up a single MWNT from the soot and connected the both ends of it to two Au/Ti electrodes patterned on a $SiO_2$ substrate (electrodes gap ~2.5 $\mu$m) using nanomanipulation system,[5,20] as shown in Fig. 4(a). We measured $I-V$ curves of our MWNTs (three samples) and commercially purified ones (four samples) with 4140B-pA meter (Hewlett Packard Co.) under the dry $N_2$ atmosphere at room temperature. Figure 4(b) shows typical $I-V$ curves of our MWNT (~20 nm in diameter) and a commercial MWNT (~90 nm in diameter). In the $I-V$ curve near the electrical breakdown,[15] the maximum current density of our single MWNT [current density ($J$) ~ $4.0\times10^{11}$ A/m$^2$ at bias voltage $V_b$ ~ 4.9 V] is about 50 times as great as that of a commercially purified MWNT ($J\sim8.0\times10^9$ A/m$^2$ at $V_b\sim4.6$ V). In a transmission electron microscope (TEM) image, we can observe no fracture of the walls for our MWNT [Fig. 4(c)]. In comparison, the commercially purified MWNT has many defects such as buckling, breakage walls, and dislocations [Fig. 4(d)]. These results suggest that the defects of MWNTs would suppress the maximum current density, since atomic disordering of walls causes scattering of electric carriers through MWNTs.

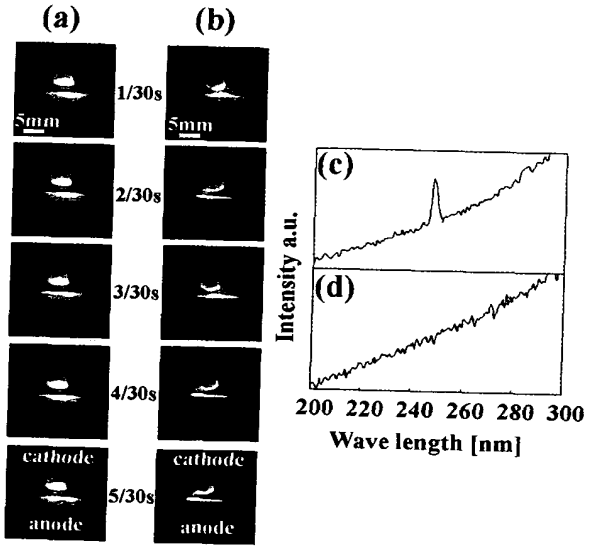


FIG. 3. (Color) Motion pictures of the arc plasma with (a) and without (b) the magnetic field. Optical emission spectra of an arc plasma with (c) and without (d) the magnetic field.

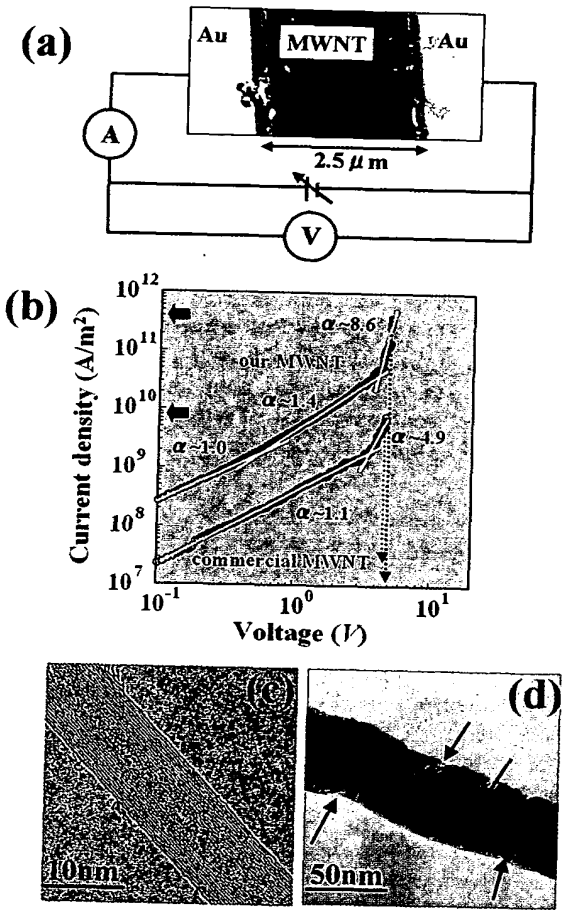


FIG. 4. (Color) (a) SEM image of the MWNT on a $SiO_2$ substrate patterned with Au/Ti electrodes. The $I-V$ measurement configuration is also shown. (b) Typical $I-V$ curves of our high-purity MWNT (red circles) and a commercial purified MWNT (blue circles). Solid arrows show maximum current densities for both MWNTs. Dashed arrows indicate electrical breakdown voltages. (c) TEM image of our high-purity MWNT. (d) TEM image of a commercial purified MWNT. Arrows show the defects in the walls of the MWNT.

In order to discuss the carrier transport mechanism, we estimated an exponent $\alpha$ of $J\propto V_b^{\alpha}$ for our MWNT and the commercially purified MWNT. As shown in Fig. 4(b), we can estimate that $\alpha$ for our MWNT is ~1.0 ($V_b$ = 0.1–0.6 V), ~1.4 ($V_b$ = 0.6–4.2 V), and ~8.6 ($V_b$ = 4.2–4.9 V). In the low-voltage region ($V_b$ = 0.1–0.6 V), our MWNT transports the carriers ohmically because of $\alpha$ ~1.0. In the middle-voltage region ($V_b$ = 0.6–4.2 V), the exponent $\alpha$(~1.4) is in good agreement with the value of 1.5 in the ballistic transportation,[8] in which the current density is approximately expressed with the Child–Langmuir

equation,[21] $J \propto V_b^{1.5}$. Therefore, the carriers would flow through the MWNT ballistically in this voltage region. In comparison, $\alpha$ for the commercial MWNTs is ~1.1 in the range of $V_b = 0.1-3.6$ V. Thus, the carrier transport through the commercial MWNT was found to be ohmic, since $\alpha$ is almost equal to a value of ohmic low ($J \propto V_b^{1.0}$). Then, the defects in the commercial MWNT [Fig. 4(d)] would scatter the carriers to interrupt the ballistic transport. In addition, with increasing $V_b$, the exponent $\alpha$ increased drastically to be ~8.6 ($V_b > 4.2$ V) for our MWNT, and ~4.9 ($V_b > 3.6$ V) for the commercial MWNT. The abrupt increasing of exponents in these high-voltage regions suggests that the carriers transport through the inner layers of MWNTs.

In conclusion, we have proposed a synthesis method of MWNTs, in which an arc discharging was controlled by a magnetic field. This method yields high-purity MWNTs (purity>95%). In the $I-V$ measurements, the maximum current density of our MWNT is about 50 times as great as that of a commercial MWNT defected with a purification process. In addition, the carriers would transport ballistically through our MWNTs. Therefore, high-purity MWNTs synthesized by our method are the most suitable for nanoscaled electric wires in device fabrication.

The authors would like to thank Professor Y. Hirotsu of the Institute of Scientific and Industrial Research, Osaka University for the use of a TEM.

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